# ANALYSIS OF BIO-OIL FROM PALM OIL WASTES THROUGH BATCH PYROLYSIS PROCESS

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## ABSTRACT

Malaysia is well known as the top largest producer of palm oil in the world. The abundance of biomass from palm oils agriculture industry would make a great benefit is they were used as a new source in fulfilling energy demand which increased year by years. The biomass can be converted into valuable product via pyrolysis process. Pyrolysis is thermal degradation either in the complete absence of oxidizing agent which is air or oxygen. The products of pyrolysis are bio-oil, char and gas. In this research, the pyrolysis of palm oil wastes (Pump Kernel Shell (PKS), Empty Fruit Bunch (EFB) and Mesocarp Fiber) was performed using a static batch reactor which being heated by a tubular furnace. Preliminary analysis was conducted using thermogravimetric analyzer (TGA) to determine the volatility, ash residue, moisture content and weight loss. 3 different physical properties were investigated on these bio-oils which are water content, pH, and viscosity. The functional groups of the product which is bio oil are identified by using Fourier Transform Infrared spectrometer (FTIR). Gas Chromatography-Mass Selectivity (GC-MS) was used to identify the component exists in the bio-oils. From the result, the pHs for all products were very acidic with pH value are 2.46, 2.53 and 2.56 respectively for Pump Kernel Shell (PKS), Empty Fruit Bunch (EFB) and Mesocarp Fiber. The viscosity values range was 33-43 cP and the water content in the bio-oils were 7-13 % weight. The result of FTIR and GC-Ms shows that, there are many complex compounds which would be a ideal for chemical feedstock and with undergoing upgrading process, can be used as fuel.

# ABSTRAK

Malaysia amat terkenal sebagai pengeluar terbesar buah kelapa sawit di dunia. Biomass yang banyak dari industri penanaman kelapa sawit boleh memberi manfaat besar jika ianya digunakan sebagai sumber tenaga baru bagi memenuhi permintaan terhadap sumber tenaga yang kian meningkat dari tahun ke tahun. ‘Biomass’ ini boleh ditukar kepada produk yang bernilai melalui proses yang dipanggil ‘Pyrolysis’. ‘Pyrolysis’ ialah penguraian termal tanpa kehadiran agen pengoksidaan iaitu udara atau lebih tepat oksigen. 3 produk yang terhasil melalui ‘Pyrolysis’ ialah ‘Bio-oil’, arang dan gas. Di dalam kajian ini, proses ‘Pyrolysis’ dilakukan terhadap hasil buangan kelapa swit ( tandan sawit kosong dan sirat Mesocarp) dengan mengunakan static reaktor ‘batch’ yang dipanaskan oleh ‘Tubular Furnace’. Analisis saringan dilakukan dengan mengunakan ‘Thermogravimetric Analyzer’ (TGA) untuk menentukan mudahruapan, arang, kandungan air dan juga berat yang hilang pada setiap sampel. 3 sifat fizikal yang berlainan bagi setiap ‘bio-oil’ dikaji iaitu kandungan air, pH dan juga kelikatan. Kumpulan berfungsi yang terdapat di dalam produk iaitu ‘bio-oil’ dikenal pasti melalui ‘Fourier Transform Infrared Spectrometer’ (FTIR).‘Gas Chromatography-Mass Selectivity’ (GC-MS) pula digunakan untuk mengenalpasti komponen-komponen yang wujud di dalam ‘bio-oil’. Daripada keputusan yang diperolehi, pH untuk semua bio-oil menunjukkan bahawa bio-oil adalah sangat berasid dengan nilai pH adalah 2.46, 2.53 and 2.56 bagi Pump Kernel Shell (PKS), Tandan Sawit Kosong (EFB) and Sirat Mesocarp. Nilai kelikatan untuk ketiga-tiga produk ‘bio-oil’ berada dalam linkungan nilai 33-43 cP dan kandungan air di dalam ‘bio-oil’ adalan 7 hingga 13 % berat.

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## LIST OF SYMBOLS

| | | |
|---|---|---|
| cm | - | Centimeter |
| °C | - | Celsius |
| Wt% | - | Weight Percentage |
| kg | - | Kilogram |
| kJ | - | Kilo Joule |
| s | - | Second |
| $CH_4$ | - | Methane |
| $CO_2$ | - | Carbon Dioxide |
| min | - | Minutes |
| T | - | Temperature |
| $M^3$ | - | Meter cubic |
| GJ | - | Giga Joule |
| Tn | - | Tonnes |
| h | - | Hour |
| mm | - | Millimeter |
| kPa | - | Kilo Pascal |
| g | - | Gram |

| | | |
|---|---|---|
| % | - | Percent |
| psi | - | Pressure unit |
| cP | - | Centi Poise |
| μm | - | Micrometer |
| mL | - | milliliter |
| He | - | Helium |

# CHAPTER 1

# INTRODUCTION

## 1.1 Research Background

Biomass refers to living and recently dead biological material that can be used as fuel. Biomass is the fourth largest source of energy in the world and particularly become an attractive energy source more many countries because of it availability and sustainability. Biomass is mainly derived from the agriculture or forestry sector. Today, various forms of biomass are consumed all over the world for energy generation. Biomass provides a clean, renewable energy source that could dramatically improve the environment, economy and energy security. The use of these materials will depend on safe state of the art, economic and technologies that are used to transform them into manageable products. One of the indigenous biomass resources in Southeast Asia is derived from the oil palm. The oil palm empty fruit bunches, fiber and shell which are generally considered as ‘waste’ are generated every year in Malaysia, with an annual increment of 5% (S. Mohamad Asri et al., 2009).

There are 3 methods in biomass conversion via thermochemical which are combustion, gasification and pyrolysis. Pyrolysis is considered to be an emerging technology for liquid oil production among these three methods in thermochemical. Pyrolysis is a thermal degradation of biomass under moderate temperature in the absence of oxygen. Pyrolysis products consist of bio-oil (condensable gas), synthetic gas (non-condensable gas), and char (Boateng et al., 2006).

Bio-oil has some advantages in transport, storage, combustion, retrofitting and flexibility in production and marketing. (Rahman, 2007). Bio-oils also referred to as biomass pyrolysis liquids, pyrolysis oils, or bio-crude oils, are dark brown, free flowing liquids with an acrid or smoky odor (Anja Oasmaa et al., 2009). They are complex mixtures of compounds that are derived from the depolymerization of cellulose, hemicellulose and lignin. Chemically, they comprise quite a lot of water, more or less solid particles and hundreds of organic compounds that belong to acids, alcohols, ketones, aldehydes, phenols, ethers, esters, sugars, furans, nitrogen compounds and multifunctional compounds ( Qiang Lu et al.,2009). Bio-oils have been regarded as promising candidates to replace petroleum fuels to be used in various thermal devices. However, bio-oils are totally different from petroleum fuels. Therefore, the successful utilization of bio-oils in terms of liquid fuels requires adequate understanding of their fuel properties. Analysis on the bio-oil physically and chemically is required in order to get better understanding about the characteristic and properties of the bio -oil.

## 1.2 Problem Statement

Projects and research in pyrolysis had been developing since 2 decade ago. Pyrolysis process produced bio-oils as its primary product and said to be a well suitable candidate to replace crude oil. In order for bio-oils to become a fuel replacement, an investigation on bio-oils properties and chemical compound in bio-oil had to be determined to find the effectiveness and suitability as a new energy source.

Devices such as diesel engines, boilers, furnaces, and gas turbines rely on spray combustion for energy conversion (T. Tzanekatis, 2008). To understand bio-oil spray behavior, a thorough knowledge of liquid properties is required. The fuel properties that most affect atomization quality and spray combustion behavior are density and viscosity. Other relevant properties of bio-oil that can affect in combustion, fueling and storage are water content and pH or acidity.

It is important to determine the physical and chemical characteristic of palm oil wastes (Pump Kernel, Empty Fruit Bunch (EFB) and Mesocarp Fiber) bio-oils from batch pyrolysis process as a potential fuel substitute. Through Fourier Transform Infrared (FTIR) and Gas Chromatography-Mass Selectivity (GC-MS), the functional group and composition in bio-oils can be analyzed. Physical properties of these bio-oil were also been investigated. 3 different physical properties were investigated on these bio-oils which are water content, pH, and viscosity.

## 1.3 Objective

1.3.1. To determine the physical properties of bio-oils which are bio-oils water content, viscosity and also acidity or pH.

1.3.2. To investigate the functional groups exist in the bio-oil via Fourier Transform Infrared and the component of bio-oils through Gas Chromatography-Mass Selectivity (GC-MS).

## 1.4 Scope of Works

1.1.1. The scope of this project is to use Palm oil wastes as the biomass sources which are Empty Fruit Bunch (EFB), Mesocarp Fibers and Pump Kernel Shell (PKS). The most abandon biomass in Malaysia come from the palm oil plantation. With production of billion tonnes per annum, palm oil wastes can be a great source for pyrolysis process in producing bio-oils.

1.1.2. The pyrolysis process is conducted in a batch process. The samples will first be filed into the reactor and then heating it until the desired temperature. A tubular reactor is use as a heating source.

1.1.3. Only bio-oils and char as a by-product will be collected. The gas by-product will be vent.

1.1.4. 3 physical properties of bio-oil which are the water content in the bio-oil, the pH and viscosity will be investigated. In determining the functional group, Fourier Transform Infrared will be used and Gas Chromatography- Mass Selectivity is use in determining chemical compound in the bio-oils.

## 1.2 Rationale and Significance

Biomass Pyrolysis is not a new technology but the importance of this technologies nowadays has become more crucial since crude oil became depleted and the environmental concern of global warming. Many researches had been conduction about the usefulness of pyrolysis and proven that this technology is worthy to be developed. Previous researches mainly focus on getting the highest production yield of bio-oils with little understanding about the fuel properties.

The focus of this project is on analysis of the bio-oil from palm oil wastes. The importance in analyzing the bio-oils is to discover studying yet understanding the physical properties and chemical components in the bio-oil in order to gain knowledge about the characteristic and benefit as a new energy source replacing the fossil fuel that is widely used in current world.

# CHAPTER 2

# LITERATURE STUDY

## 2.0 Renewable Energy

With the increasing evidence of global warming, unstable crude oil's prices in world market, depletion in current reservation with only few effort in finding new crude oil's reservoir source and idea of being carbon neutral becoming more prominent, the increase in interest in renewable energy is growing rapidly. Renewable energy takes on many forms, and usually describes using natural resources that won't run out.

There are several main renewable energy technologies in use, most of which are directly or indirectly due to the sun such as wind turbine, solar power and power generation from sea wave. But these kinds of renewable energy is not commercially used and based on geography of certain places for example, in sunny climates, it makes more sense to create renewable energy from solar panels, whereas in coastal areas, it may be more efficient and effective to use wave or tidal power.

To overcome these, biomass seems be more promising as a source of renewable energy as it is more reliable and sustainable source. Biomass can be found anywhere and can be replaced. As the need for alternative forms of energy become more important, biomass can play a bigger part for the production of fuel and electricity generations.

## 2.1 Biomass

Biomass refers to living and recently dead biological material that can be used as fuel or for industrial production. Most commonly, biomass refers to plant matter grown to generate electricity or produce biofuel, but it also includes plant or animal matter used for production of fibers, chemicals or heat. Biomass may also include biodegradable wastes that can be burnt as fuel. Fossil fuels such as coal and oil are not considered to be biomass as they are not recently dead, nor were they produced especially to become biomass.

Biomass is carbon based and is composed of a mixture of organic molecules containing hydrogen, usually including atoms of oxygen, often nitrogen and also small quantities of other atoms, including alkali, alkaline earth and heavy metals. These metals are often found in functional molecules such as the porphyrins which include chlorophyll which contains magnesium.

The carbon used to construct biomass is absorbed from the atmosphere as carbon dioxide ($CO_2$) by plant life, using energy from the sun.

Plants may subsequently be eaten by animals and thus converted into animal biomass. However the primary absorption is performed by plants.

If plant material is not eaten it is generally either broken down by microrganisms or burned:

- If broken down it releases the carbon back to the atmosphere, mainly as either carbon dioxide ($CO_2$) or methane ($CH_4$), depending upon the conditions and processes involved.
- If burned the carbon is returned to the atmosphere as $CO_2$.

These processes have happened for as long as there have been plants on Earth and is part of what is known as the carbon cycle.

### 2.1.1 Biomass Major Component

Biomass consists of three major components: cellulose, hemicellulose and lignin. Cellulose is a straight and stiff molecule with a polymerization degree of approximately 10.000 glucose unite (C6 sugar) Hemicellulose are polymers built C5, C6 sugars with a polymerisation degree of about 200 sugar units. Both cellulose and hemicellulose can be vapored with negligible char formation at temperatures above 500 "C. Lignin is a three dimensional branched polymer composed phenolic units. Due to the aromatic content of lignin, it degrades slowly on heating and contributes to a major fraction of the char formation. In addition to the major cell wall composition like cellulose, hemicellulose and lignin, biomass often contains varying amounts of species called "extractives". These extractives, which are soluble in polar or no polar solvents, consists of terpenes, fatty acids, aromatic compounds and volatile oil.

### 2.1.2 Difference between Biomass and Fossil Fuels

Fossil fuel such as coal, oil and gas are also derived from biological materials, however material that absorbed $CO_2$ from the atmosphere many millions of year ago. As fuel, they offer high energy density, but making use of that energy involves burning the fuel, with the oxidation of the carbon to carbon dioxide and the hydrogen to water (vapor). Unless they are captured and stored, these combustion products are usually released to the atmosphere, returning carbon sequestered millions years ago and thus contributing to increase $CO_2$ atmospheric concentrations.

Biomass takes carbon out of the atmosphere while it is growing and returns it as it is burned. If it is managed on a sustainable basis, biomass is harvested as part of a constantly replenished crop. This is either during woodland or arboricultural management or coppicing or as part of a continuous program of replanting with new growth taking up $CO_2$ from the atmosphere at the same time as it is released by combustion of the previous harvest. This maintains a closed carbon cycle with no net increase in atmospheric $CO_2$ level.

### 2.1.3 Categories of Biomass Material

Within the Biomass definitions, biomass for energy can include a wide range of materials. Biomass had been categorized for easy description. There are 5 basic categories of biomass materials as listed in table 2.1.

**Table 2.1**: Categories of Biomass

| Biomass Categories | |
|---|---|
| Virgin Wood | Forestry, Arboricultural, Wood processing plant |
| Energy Crops | High yield crops grown specifically for energy applications |
| Agricultural Residues | Residues from Agriculture, Harvesting or Processing |
| Food Waste | Food and drink manufacture, Preparation and processing and Post customers waste |
| Industrial Waste and Co-Products | Manufacturing and Industrial Processes |

### 2.1.4 Biomass In Malaysia

The oil palm industry in Malaysia started 80 years ago in a modest way. Today it is the largest in agricultural plantation sector, exceeding rubber plantation by more than double in area planted. Based on the researched from the World Wildlife Fund

(WWF), Malaysia is currently the world's largest producer of palm oil, contributing of 50.9% of total global production.

In terms of hectare, the total area under oil palm cultivation is over 2.65 million hectares, producing over 8 million tonnes of oil annually. The oil consists of only 10% of the total biomes produced in the plantation. The remainder consists of huge amount of lignocellulosic materials such as oil palm fronds, trunks and empty fruit bunches. The projection figures of these residues are as follows:

- 7.0 million tonnes of oil palm trunks
- 26.2 million tonnes of oil palm fronds
- 23% of Empty Fruit Bunch (EFB) per tonne of Fresh Fruit Bunch (EFB) processed in oil palm mill

Based on the above, Malaysia therefore has a great potential in turning its abundance supply of palm oil industry by products into value added products.

**Figure 2.1**: Empty Fruit Bunch Wastes (MPOA, 2003)

Under the present scenario, Malaysia can no longer remain idle and complacent in its position as the top grower and supplier of palm oil. In view of the escalating challenge posed by the other oil producing countries, Malaysia has to change its objective of being a world producer of palm oil to amongst others a leader in converting biomass waste into value-added products. Malaysia has therefore to seriously resort in aggressive R&D to support its ambition.

The major contributor of biomass in Malaysia that has potential to generate energy is in palm oil industry where most of the waste is:

– Empty fruit bunches (EFB)
– Palm oil mill effluent (POME)
– Mesocarp fiber
– Palm kernel shells
– Palm kernel cake (residue)

As been stated above, the types and amounts of these biomass generated in 2005 are tabulated in table below.

**Table 2.2**: Biomass Generated in 2005 (A.B. Nasrin, 2008)

| Palm biomass generated in year 2005 | | | | |
|---|---|---|---|---|
| Biomass | Quantity, million tonnes, * | Moisture Content, %** | Calorific Value, kJ/kg** | Main uses |
| Fibre | 9.66 | 37.00 | 19068 | Fuel |
| Shell | 5.20 | 12.00 | 20108 | Fuel |
| Empty Fruit Bunches | 17.08 | 67.00 | 18838 | Mulch |
| Palm Kernel Expeller | 2.11 | 3.00 | 18900 | Animal feed |

### 2.1.5 Biomass Conversion

There are 2 method for biomass conversion with are the Biological Method and Thermochemical Method. Biomass such as forest residue, agricultural residue and organic food processing waste can be converted to chemical and energy product via either biological (Lin and Tanaka, 2006) or thermochemical processes (Caputo et al., 2005). Biological conversion of low valued lignocellulosic tp commercial chemical and energy products, particularly ethanol, still face challenges in low economy and efficiencies (Lin and Tanaka, 2006). Thermochemical conversion provides a competitive ways to produce chemicals and energy products from low value and highly distributed biomass resources with large variation of properties. Combustion, Pyrolysis and Gasification are 3 main thermochemical conversion methods (Knoef et al., 2005)

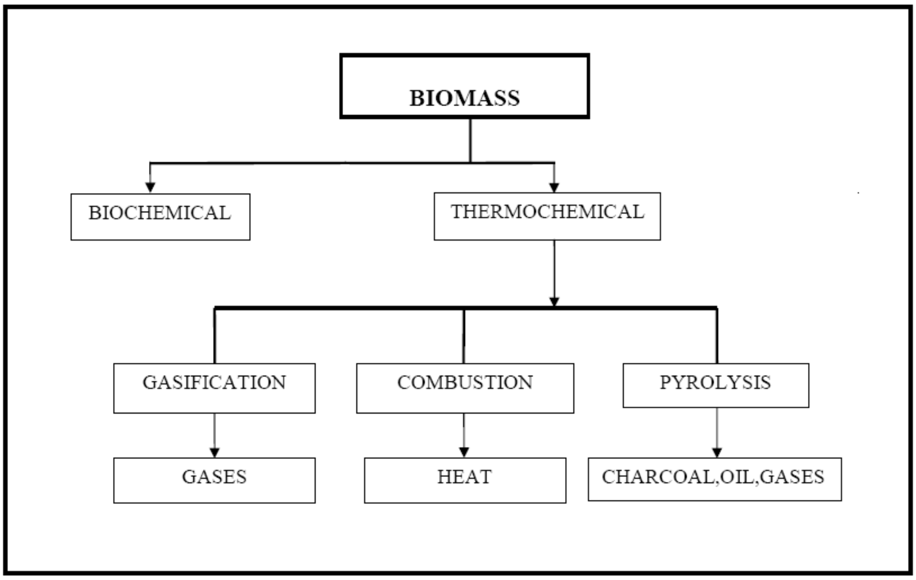


**Figure 2.2**: Main Processes of Biomass Conversion

Figure 2.2 summarized the thermochemical method and the products from the process. Combustion is the conventional of chemical energy stored in an organic matter into heat, generating carbon dioxide and water as the final products. Combustion usually produces hot gas at temperature around 800°C to 1000°C. Pyrolysis is the conversion of biomass into liquid, solid and gaseous fraction by heating the biomass in the absent of air or oxygen at relatively low temperature around 300°C to 800°C. Gasification is the partial oxidation of organic matter at a high temperature to convert the organic matter into a combustible gas mixture called syngas, which mainly consist of carbon monoxide, hydrogen, methane and carbon dioxide. Gasifiers are operate at approximately 800°C to

1000°C although a non-catalytic entrained flow gasifier could be operated at a temperature as high as 1300°C. Among 3 processes in Thermochemical method, Pyrolysis is said to be the most suitable method in providing substituted energy source as it can produce bio-oils.

## 2.2 Pyrolysis

Pyrolysis is thermal degradation either in the complete absence of oxidizing agent, or with such a limited supply that gasification does not occur to an appreciable extent or may be described as partial gasification. Relatively low temperatures are employed of 500 to 800 °C, compared to 800 to 1000 °C in gasification. Three products are usually produced: gas, pyrolysis oil and charcoal, the relative proportions of which depend very much on the pyrolysis method, the characteristics of the biomass and the reaction parameters.

### 2.2.1 History of Pyrolysis

Direct Combustion is the old way of using biomass. The biomass is completely transformed into heat, but the efficiency is just about 10 percent. The gasification pushes to the maximum level the cracking of biomass by completely transforming it into a combustible gas before burning it. The charcoal production, the slow pyrolysis of wood at temperature 500 °C is a process that charcoal makers have exploited for thousands years. Charcoal is a smokeless fuel which is still used for heating purposes. It first technological use can be dated back to the Iron Age when charcoal was used in ore melting to produce iron.

### 2.2.2 Classification of Pyrolysis

Pyrolysis has been practiced for centuries for production of charcoal. This requires relatively slow reaction at very low temperatures to maximize solid yield. More recently, studies into the mechanisms of pyrolysis have suggested ways of substantially changing the proportions of the gas, liquid and solid products by changing the rate of heating, temperature and residence time.

High heating rates, of up to a claimed 1000 °C/s or even 10000 °C/s, at temperature below about 650 °C and with rapid quenching, causes the liquid intermediate products of pyrolysis to condense before further reaction breaks down higher molecular weight species into gaseous products. The high reaction rates also minimize char formation, and under some condition no char is apparently formed. At high maximum temperature, the major product is gas. Pyrolysis at these high heating rates is known as fast or flash pyrolysis according to the heating rate and residence time, although the distinctions are blurred. Other work has attempted to exploit the complex degradation mechanisms by carry out pyrolysis in unusual environment. The main pyrolysis variants are listed in Table 2.2 and the characteristics of the main models of pyrolysis are summarized into Table 2.3.

**Table 2.3**: Pyrolysis Technology Variant (FOA, 2009)

| Tech. | Residence time | Heating rate | Temperature °C | Products |
|---|---|---|---|---|
| carbonation | days | very low | 400 | charcoal |
| Conventional | 5-30 min | low | 600 | oil, gas, char |
| Fast | 0.5-5s | very high | 650 | bio-oil |
| Flash-liquid | < 1 s | high | < 650 | bio-oil |
| Flash-gas | < 1 s | high | < 650 | chemicals, gas |
| Ultra | < 0.5 | very high | 1000 | chemicals, gas |
| Vacuum | 2-30s | medium | 400 | bio-oil |
| Hydro-pyro. | < 10s | high | < 500 | bio-oil |
| Methano-pyro. | < 10s | high | > 700 | chemicals |